

EFFICIENT ELECTRODE ASSEMBLY DESIGN FOR CELLS
WITH ALKALI METAL ANODES

5 CROSS REFERENCE TO RELATED APPLICATION

The present application claims priority from provisional application Serial No. 60/458,173, filed March 27, 2003.

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BACKGROUND OF THE INVENTION

Implantable ventricular cardiac defibrillators typically use lithium/silver vanadium oxide (Li/SVO) 15 electrochemical cells as their power source. For the implantable medical device itself, it is preferable that the device be relatively small in size, quick in response to the patient's medical needs, promote long device service life, and the like. Therefore, when cells are 20 built for implantable medical applications, special electrode assembly designs are needed to meet all of these requirements. Additionally, for cells powering cardiac defibrillators, a large electrode surface area is required to provide the needed power capability. An efficient cell 25 package is also needed to achieve the highest capacity in the smallest volume.

In a conventional electrode assembly for Li/SVO cells, the cathode active material is pressed, coated or otherwise contacted to both sides of a foil or screen 30 cathode current collector to provide the cathode

electrode. Lithium as the anode active material in the form of a foil is pressed onto both sides of an anode current collector to form the anode electrode. The anode and the cathode electrodes are then placed against each 5 other with one or two layers of intermediate separator material. The final electrode assembly is typically in the form of a prismatic plate design or a jellyroll design. An example of the conventional prismatic plate design is disclosed in U.S. Patent No. 5,147,737 to Post 10 et al. An example of a conventional jellyroll design is disclosed in U.S. Patent No. 5,439,760 to Howard et al.

To further illustrate this point, FIG. 1 shows a conventional prismatic or jellyroll electrode assembly. The electrode assembly 10 includes an anode electrode 12 and a cathode electrode 14 segregated from each other by separator sheets 16. The anode electrode comprises an anode active material 18, such as lithium, contacted to both sides of an anode current collector 20, such as of nickel. The cathode electrode 14 comprises a cathode active material 22 contacted to both sides of a cathode current collector 24, such as of titanium. The outermost winds or plates are of an anode electrode directly adjacent to a casing sidewall 26. Separator sheets 16 reside between the electrode units and the outermost anode 25 electrode structures. Finally, the entire electrode assembly is contained in a polymeric insulator bag 28 that is then inserted into the casing 26.

The anode electrode is electrically connected to the conductive casing 26 as the negative electrode terminal. 30 The cathode electrode is electrically connected to a

terminal lead insulated from the casing by a glass-to-metal seal (not shown). The general structure of a glass-to-metal seal is well known by those skilled in the art and does not necessarily form a basis for the present

5 invention.

Since the electrode assembly thickness is the sum of the thickness of each component, the fewer the non-active component layers, the more volume for the active components and, consequently, the higher the cell's

10 volumetric capacity. Therefore, the packaging efficiency of the prior art electrode assembly can be further improved by having the casing wall serve as part of the anode current collector.

15 SUMMARY OF THE INVENTION

The present invention improves the performance of lithium electrochemical cells by providing a new electrode assembly based on a convention prismatic or jelly roll configuration. Regardless of whether the cell is built in a case-positive or a case-negative design, the casing sidewalls serve as part of the anode or the cathode current collector, respectively. This eliminates some of the non-active or passive material of the conventional cell designs. The present cells are particularly useful for powering implantable medical devices, such as a cardiac defibrillator, pacemakers, implantable drug pumps, and the like.

30 These and other aspects and advantages of the present invention will become increasingly more apparent to those

skilled in the art by reference to the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

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FIG. 1 is a cross-sectional view of a prior art electrochemical cell including either a prismatic plate or a jellyroll electrode assembly.

10 FIG. 2 is a cross-sectional view of a present invention electrochemical cell including either a prismatic plate or a jellyroll electrode assembly.

DETAILED DESCRIPTION OF THE INVENTION

15 An electrochemical cell according to the present invention must have sufficient energy density and discharge capacity in order to be a suitable power source for implantable medical devices. Such cells comprise an anode of a metal selected from Groups IA, IIA and IIIB of 20 the Periodic Table of the Elements. These anode active materials include lithium, sodium, potassium, etc., and their alloys and intermetallic compounds including, for example, Li--Si, Li--Al, Li--B and Li--Si--B alloys and intermetallic compounds. The preferred anode comprises 25 lithium. An alternate anode comprises a lithium alloy such as a lithium-aluminum alloy. The greater the amounts of aluminum present by weight in the alloy, however, the lower the energy density of the cell.

30 The form of the anode may vary, but preferably it is a thin metal sheet or foil of the anode metal, pressed or

rolled on a metallic anode current collector, i.e., preferably comprising titanium, titanium alloy or nickel, to form an anode component. Copper, tungsten and tantalum are also suitable materials for the anode current 5 collector. In the exemplary cell of the present invention, the anode component has an extended tab or lead of the same material as the anode current collector, i.e., preferably nickel or titanium, integrally formed therewith such as by welding and contacted by a weld to a cell case 10 of conductive metal in a case-negative electrical configuration. Alternatively, the anode may be formed in some other geometry, such as a bobbin shape, cylinder or pellet to allow an alternate low surface cell design.

The electrochemical cell of the present invention 15 further comprises a cathode of electrically conductive material that serves as the other or counter electrode. The cathode is preferably of solid materials and the electrochemical reaction at the cathode involves conversion of ions that migrate from the anode to the 20 cathode into atomic or molecular forms. The solid cathode may be of a carbonaceous chemistry or comprise a metal element, a metal oxide, a mixed metal oxide, a metal sulfide, and combinations thereof. The metal oxide, the mixed metal oxide and the metal sulfide are formed by the 25 chemical addition, reaction, or otherwise intimate contact of various metal oxides, metal sulfides and/or metal elements, preferably during thermal treatment, sol-gel formation, chemical vapor deposition or hydrothermal synthesis in mixed states. The active materials thereby 30 produced contain metals, oxides and sulfides of Groups,

IB, IIB, IIIB, IVB, VB, VIB, VIIIB and VIII, which includes the noble metals and/or other oxide and sulfide compounds. A preferred cathode active material is a reaction product of at least silver and vanadium.

5 One preferred mixed metal oxide is a transition metal oxide having the general formula $SM_xV_2O_y$ where SM is a metal selected from Groups IB to VIIIB and VIII of the Periodic Table of Elements, wherein x is about 0.30 to 2.0 and y is about 4.5 to 6.0 in the general formula. By way of illustration, and in no way intended to be limiting, one exemplary cathode active material comprises silver vanadium oxide having the general formula $Ag_xV_2O_y$ in any one of its many phases, i.e., β -phase silver vanadium oxide having in the general formula x = 0.35 and y = 5.8, γ -phase silver vanadium oxide having in the general formula x = 15 0.80 and y = 5.40 and ϵ -phase silver vanadium oxide having in the general formula x = 1.0 and y = 5.5, and combinations and mixtures of phases thereof. For a more detailed description of such cathode active materials reference is made to U.S. Patent No. 4,310,609 to Liang et al., which is assigned to the assignee of the present invention and incorporated herein by reference.

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25 Another preferred composite transition metal oxide cathode active material is copper silver vanadium oxide (CSVO), which is described U.S. Patent Nos. 5,472,810 to Takeuchi et al. and 5,516,340 to Takeuchi et al. Both are assigned to the assignee of the present invention and incorporated herein by reference.

Another cathode active material is a carbonaceous compound prepared from carbon and fluorine, which includes graphitic and nongraphitic forms of carbon, such as coke, charcoal or activated carbon. Fluorinated carbon is 5 represented by the formula $(CF_x)_n$ wherein x varies between about 0.1 to 1.9 and preferably between about 0.5 and 1.2, and $(C_2F)_n$ wherein the n refers to the number of monomer units which can vary widely.

Additional cathode active materials include V_2O_5 , 10 MnO_2 , $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, TiS_2 , Cu_2S , FeS , FeS_2 , Ag_2O , Ag_2O_2 , CuF_2 , Ag_2CrO_4 , copper oxide, copper vanadium oxide, and mixtures thereof.

Before fabrication into an electrochemical cell, the cathode active material is preferably mixed with a binder 15 material such as a powdered fluoro-polymer; more preferably powdered polytetrafluoroethylene or powdered polyvinylidene flouride present at about 1 to about 5 weight percent of the cathode mixture. Further, up to about 10 weight percent of a conductive diluent is 20 preferably added to the cathode mixture to improve conductivity. Suitable materials for this purpose include acetylene black, carbon black and/or graphite or a metallic powder such as powdered nickel, aluminum, titanium and stainless steel. The preferred cathode 25 active mixture thus includes a powdered fluoro-polymer binder present at about 3 weight percent, a conductive diluent present at about 3 weight percent and about 94 weight percent of the cathode active material.

Cathode components for incorporation into an 30 electrochemical cell according to the present invention

may be prepared by rolling, spreading or pressing the cathode active materials onto a suitable current collector selected from the group consisting of stainless steel, titanium, tantalum, platinum, gold, aluminum, cobalt 5 nickel alloys, nickel-containing alloys, highly alloyed ferritic stainless steel containing molybdenum and chromium, and nickel-, chromium- and molybdenum-containing alloys. The preferred current collector material is titanium. When the active material is a fluorinated 10 carbon, the titanium cathode current collector has a thin layer of graphite/carbon material, iridium, iridium oxide or platinum applied thereto. Cathodes prepared as described above may be in the form of one or more plates operatively associated with at least one or more plates of 15 anode material, or in the form of a strip wound with a corresponding strip of anode material in a structure similar to a "jellyroll".

In order to prevent internal short circuit 20 conditions, the cathode is separated from the Group IA, IIA or IIIB anode by a suitable separator material. The separator is of electrically insulative material, and also is chemically unreactive with the anode and cathode active materials and both chemically unreactive with and insoluble in the electrolyte. In addition, the separator 25 material has a degree of porosity sufficient to allow flow there through of the electrolyte during the electrochemical reaction of the cell. Illustrative separator materials include fabrics woven from fluoropolymeric fibers including polyvinylidene fluoride, 30 polyethylenetetrafluoroethylene, and

polyethylenechlorotrifluoroethylene used either alone or laminated with a fluoropolymeric microporous film, non-woven glass, polypropylene, polyethylene, glass fiber materials, ceramics, a polytetrafluoroethylene membrane 5 commercially available under the designation ZITEX (Chemplast Inc.), a polypropylene membrane commercially available under the designation CELGARD (Celanese Plastic Company, Inc.), a membrane commercially available under the designation DEXIGLAS (C.H. Dexter, Div., Dexter 10 Corp.), and a membrane commercially available under the designation TONEN.

FIG. 2 shows a prismatic or jellyroll electrode assembly according to the present invention. The electrode assembly 30 includes an anode electrode 32 and a 15 cathode electrode 34 segregated from each other by separator sheets 36. The anode electrode preferably comprises lithium 38 contacted to both sides of a nickel anode current collector 40. The cathode electrode 34 comprises one or more of the previously described cathode 20 active materials 42 contacted to both sides of a cathode current collector 44, such as of titanium. The outermost winds or plates are of an anode electrode directly adjacent to a casing sidewall 46. Separator sheets 36 reside between the electrode units and the outermost anode 25 electrodes. Finally, the entire electrode assembly is contained in a polymeric insulator bag 20 that is then inserted into the casing 38.

Unlike the conventional cell construction shown in FIG. 1, the outermost anode electrodes use the casing 30 sidewalls 46 as part of their current collector. In a

jellyroll electrode assembly, a lithium foil is press contacted to at least one side of an anode current collector. A portion of the lithium foil extends out beyond an edge of the anode current collector. This 5 portion is then press contacted to the inner surface of the casing sidewalls. In a prismatic design, one of the plates without a current collector is contacted to the inner surface of the casing sidewall.

Referring back to FIG. 1, in a conventional prismatic 10 or jellyroll electrode assembly in a case-negative cell design, there are $n \geq 1$ electrode units of cathode electrode/separator/anode electrode/separator/cathode electrode. This is shown where $n = 1, 2, 3, 4, 5$, etc. In this cell design, the number of layers for each 15 component is calculated as:

no. of cell case wall layers = 2

no. of insulator bag layers = 2

20 no. of separator layers = $4n+6$

no. of anode layers = $2n+2$

25 no. of anode current collector layers = $n+2$

no. of cathode layers = $4n$

no. of cathode current collector layers = $2n$

Thus, assuming $n = 1$ in FIG. 1, there are two casing wall layers, two insulator bag layers, ten separator layers, six anode lithium layers, three anode current collector layers, four cathode active material layers, and .
5 two cathode current collector layers.

As shown in FIG. 2, in the present invention cells, whether of a prismatic or a jellyroll case-negative design, there are $n \geq 1$ electrode units of cathode electrode/separator/anode electrode/separator/cathode electrode where $n = 1, 2, 3, 4, 5$, etc. However, since the casing sidewall serves as part of the anode electrode current collector, there are two less layers of insulator bag, two less layers of separator, and two less anode current collector screens. In this cell design, the
10 number of layers for each component is calculated as:
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no. of cell case wall layers = 2

no. of separator layers = $4n+4$

20 no. of anode layers = $2n+2$

no. of anode current collector layers = n

25 no. of cathode layers = $4n$

no. of cathode current collector layers = $2n$

This means that the volumetric energy density of cells according to the present invention is higher than that of cells having the conventional electrode assembly shown in FIG. 1. This also holds true for cells built in 5 a case-positive design having the casing sidewalls serving as part of the cathode current collector.

In a case-negative design, since lithium is the best heat conductor in the electrode assembly, including the cathode active material, electrolyte, separator, and 10 insulator bag, contact between the lithium metal and the casing sidewall allows for more efficient heat dissipation from the cell to the ambient environment under abusive conditions. This includes short circuit or over charge and over discharge conditions. As a result, the cell of 15 the present invention is relatively safer than the cell with the conventional electrode design shown in FIG. 1.

In a case-positive design, the cathode active material is contacted to the casing by any one of a number of techniques including pressing a powdered mixture of the 20 cathode active mixture to the inner surface of the sidewalls. Other means include forming a freestanding sheet of the cathode active mixture as described in U.S. Patent Nos. 5,435,874 and 5,571,640, both to Takeuchi et al., that is then press contacted to the inner surface of 25 the casing sidewalls, or by a thermal spray deposited technique, as described in U.S. Patent No. 5,716,422 to Muffoletto et al. These patents are assigned to the assignee of the present invention and incorporated herein by reference. In either the jellyroll or prismatic 30 electrode assembly, there is a conductor extending from

the casing sidewall or the electrode active material contacted thereto, whether of the anode or the cathode, to the other portions of the same polarity electrode not in direct contact with the casing.

5 The electrochemical cell further includes a nonaqueous, ionically conductive electrolyte that serves as a medium for migration of ions between the anode and the cathode electrodes during electrochemical reactions of the cell. The electrochemical reaction at the electrodes 10 involves conversion of ions in atomic or molecular forms that migrate from the anode to the cathode. Thus, the nonaqueous electrolyte is substantially inert to the anode and cathode materials, and exhibits those physical properties necessary for ionic transport, namely, low 15 viscosity, low surface tension and wettability.

 A suitable electrolyte has an inorganic, ionically conductive salt dissolved in a nonaqueous solvent, and more preferably, an ionizable alkali metal salt dissolved in a mixture of aprotic organic solvents comprising a low 20 viscosity solvent and a high permittivity solvent. The salt serves as the vehicle for migration of the anode ions to intercalate or react with the cathode active materials and preferably, is similar to the alkali metal comprising the anode. In the case of an anode comprising lithium, 25 suitable salts include LiPF₆, LiBF₄, LiAsF₆, LiSbF₆, LiClO₄, LiO₂, LiAlCl₄, LiGaCl₄, LiC(SO₂CF₃)₃, LiN(SO₂CF₃)₂, LiSCN, LiO₃SCF₃, LiC₆F₅SO₃, LiO₂CCF₃, LiSO₆F, LiB(C₆H₅)₄ and LiCF₃SO₃, and mixtures thereof.

 Useful low viscosity solvents include esters, linear 30 and cyclic ethers and dialkyl carbonates such as

tetrahydrofuran (THF), methyl acetate (MA), diglyme, triglyme, tetraglyme, dimethyl carbonate (DMC), 1,2-dimethoxyethane (DME), 1,2-diethoxyethane (DEE), 1-ethoxy,2-methoxyethane (EME), ethyl methyl carbonate, 5 methyl propyl carbonate, ethyl propyl carbonate, diethyl carbonate, dipropyl carbonate, and mixtures thereof. Suitable high permittivity solvents include cyclic carbonates, cyclic esters, cyclic amides and a sulfoxide such as propylene carbonate (PC), ethylene carbonate (EC), 10 butylene carbonate, acetonitrile, dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide, γ -valerolactone, γ -butyrolactone (GBL), N-methyl-pyrrolidinone (NMP) and mixtures thereof. In the present invention, the preferred anode active material is lithium metal, the preferred 15 cathode active material is SVO and the preferred electrolyte is 0.8M to 1.5M LiAsF₆ or LiPF₆ dissolved in a 50:50 mixture, by volume, of propylene carbonate and 1,2-dimethoxyethane.

The metallic casing may comprise materials such as 20 stainless steel, mild steel, nickel-plated mild steel, titanium, tantalum or aluminum, but not limited thereto, so long as the metallic material is compatible for use with components of the cell. The cell header or lid comprises a metallic disc-shaped body with a first hole to 25 accommodate the glass-to-metal seal/terminal pin feedthrough and a second hole for electrolyte filling. The glass used is of a corrosion resistant type having up to about 50% by weight silicon such as CABAL 12, TA 23, FUSITE 425 or FUSITE 435. The positive terminal pin

feedthrough preferably comprises titanium although molybdenum, aluminum, nickel alloy, or stainless steel can also be used. The cell header is typically of a material similar to that of the casing. The positive terminal pin 5 supported in the glass-to-metal seal is, in turn, supported by the header, which is welded to the casing containing the electrode assembly. The cell is thereafter filled with the electrolyte solution described hereinabove and hermetically sealed such as by close-welding a 10 stainless steel ball over the fill hole, but not limited thereto.

It is appreciated that various modifications to the inventive concepts described herein may be apparent to 15 those skilled in the art without departing from the spirit and the scope of the present invention defined by the hereinafter appended claims.